

# PATENT ABSTRACTS OF JAPAN

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(22)Date of filing : 14.09.1993 (72)Inventor : MATSUKURA MINORU

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## (54) PRODUCTION OF CERIC OXIDE

### (57)Abstract:

**PURPOSE:** To easily obtain the white tone ceric oxide having high specific surface area, low in reduction of the specific surface area under high temp. by baking monoxy cerium carbonate obtained by subjecting to moisture and heat treatment cerium carbonate.

**CONSTITUTION:** Cerium carbonate is put in a constant temp. constant humidity vessel or the drying vessel, etc., introduced steam, and is subjected to moisten and heat-treatment within the temp. range of 60-100°C, under the high humidity of  $\geq 80\%$  relative humidity and for  $\geq 1$  hour, and acicular or spherical monoxy cerium carbonate is obtained. Then, the monoxy cerium carbonate is burnt at 300-650°C for 1-4 hour to produce the ceric oxide having  $\geq 140\text{m}^2/\text{g}$  specific surface area.

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## LEGAL STATUS

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**CLAIMS**

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[Claim(s)]

[Claim 1] The manufacture approach of the second cerium of oxidation characterized by calcinating after performing humidification heat-treatment in a 60-100-degree C temperature requirement and using a carbonic acid cerium as a mono-oxy-carbonic acid cerium under high humidity of 80% or more of relative humidity.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

#### [0001]

[Industrial Application] This invention relates to offering in detail the second cerium of oxidation by which the fall of specific surface area was stabilized few also in the high temperature field, and the second cerium of oxidation near white as a color tone about the manufacture approach of the second cerium of oxidation.

#### [0002]

[Description of the Prior Art] Conventionally, the second cerium of oxidation is used in large quantities as the catalyst for exhaust gas clarification, a silicone rubber filler, abrasives, etc., for example, is set in the catalyst field. Absorb oxygen by the oxidizing atmosphere and the property of the second cerium of oxidation of emitting oxygen by reducing atmosphere is used. HC, CO, and NOx It is used as an additive which raises thermal resistance, without performing receiving improvement in the rate of purification, and reducing rubber reinforcement in a silicone rubber filler. Such second conventional cerium of oxidation is manufactured by the approach of adding oxalic acid or ammonium bicarbonate in the nitrate solution or hydrochloride solution of a cerium, and usually washing, drying and calcinating the precipitate obtained a RO exception etc. However, although the second conventional cerium of oxidation manufactured by said approach etc. had the specific surface area about 100m<sup>2</sup> / g, when [ in which specific surface area falls to below 10m<sup>2</sup> / g by 800 degree-C baking ] adding and using it for silicone rubber further, since whenever [ yellow / of the second cerium of oxidation ] was high, it had the fault that the color of rubber came seemingly to be yellow. Moreover, since the polish capacity of the second cerium of oxidation used for abrasives is greatly influenced by the mechanochemical part (surface activity), high specific-surface-area-ization in the about 800-1000-degree C usual burning-temperature region is desired.

#### [0003]

[Problem(s) to be Solved by the Invention] In order to use for the above applications and to raise the engine performance etc. further, it is required that a color tone should be brought close to white at the thing list whose fall of a still higher specific surface area and the specific surface area in an elevated temperature is stable few as a property of the second cerium of oxidation.

#### [0004]

[Means for Solving the Problem] As a result of examining many things that the above-mentioned technical problem should be solved, after this invention person performed humidification heat-treatment in the 60-100-degree C temperature requirement and used the carbonic acid cerium as the mono-oxy-carbonic acid cerium under high humidity of 80% or more of relative humidity, he found out the manufacture approach of the second cerium of oxidation characterized by calcinating.

[0005] First, it describes about the carbonic acid cerium which is a raw material. The carbonic acid cerium is marketed and it can also perform using it in this invention. It is as follows supposing an example which manufactures a carbonic acid cerium is shown. That is, a cerium-nitrate water solution and an ammonium bicarbonate water solution are mixed first, and carbonic acid cerium precipitate is

obtained. Under the present circumstances, a mixed sequence foreword may add an ammonium bicarbonate water solution in a cerium-nitrate water solution, or may carry out addition mixing of the cerium-nitrate water solution at an ammonium bicarbonate water solution. 30-200g /of concentration of this cerium-nitrate water solution is [ 1. ] the range of 100-150g/l. especially preferably preferably.

Moreover, as for the mixed rate of a cerium-nitrate water solution and an ammonium bicarbonate water solution, it is desirable that it is the range of 1:1.4-3 in the weight ratio of the cerium nitrate contained in each water solution and ammonium bicarbonate. Under the present circumstances, the carbonic acid ceriums obtained are  $Ce_2 3 (CO_3)$  and  $xH_2 O$  ( $x=1-8$ ) in a trivalent cerium.

[0006] This invention next performs humidification heat-treatment for the carbonic acid cerium obtained as mentioned above or a commercial thing under high humidity of 80% or more of relative humidity in a 60-100-degree C temperature requirement. By this processing, a needlelike or spherical mono-oxy-carbonic acid cerium [ $Ce_2 O(CO_3)_2$  and  $xH_2 O$  ( $x=1-6$ )] generates from a 6 corner-guard-like carbonic acid cerium.

[0007] The oven which introduced a thermo hygrometer and steam can perform the above-mentioned humidification heat-treatment, and the processing time has 1 desirable hours or more. Since the generation rate of a mono-oxy-carbonic acid cerium will fall probably because the desorption for surface water arises and most will serve as basic carbonates, such as  $Ce(OH)_2 (CO_3)$  and  $xH_2 O$ , before desorption of water of crystallization if a mono-oxy-carbonic acid cerium does not generate but 100 degrees C is exceeded probably because water of crystallization cannot \*\*\*\* easily when the temperature of humidification desiccation processing is less than 60 degrees C, it is necessary to consider as the above-mentioned temperature requirement. Moreover, since an amorphous part appears from a carbonic acid cerium like [ if relative humidity is less than 80%, probably because the amount of surface water will \*\*\*\* before desorption of water of crystallization ] the usual desiccation processing, it is not desirable.

[0008] Next, although the second cerium of oxidation is obtained by calcinating the mono-oxy-carbonic acid cerium made to generate, it is 300-550 degrees C more preferably, and 1 - 4 hours of firing time are desirable [ this burning temperature has desirable 300-650 degrees C, and ]. It is completely  $CeO_2$  even if it lengthens firing time, when burning temperature is less than 300 degrees C.  $CeO_2$  obtained when it was hard to change and 550 degrees C was exceeded Since specific surface area is small in comparison, it is not desirable.

[0009] The second cerium of oxidation obtained in this invention has more than  $140m^2 / g$ , and a large specific surface area, and it has an elevated temperature and at least 700 degrees C or more of properties with especially few falls of specific surface area, and is the thing of the high color tone of a whiteness degree. Moreover, that configuration is also a needle, a globular shape, a cube, etc., in the case of a globular shape and a cube, a path and one side are 20 micrometers or less, respectively, and when needlelike, a size is not limited for them to this value, although 10 micrometers or less and die length have [ three or more ] 60 micrometers and a common aspect ratio. Even if it remains as it is, it can also be used, but in mixing with a zirconium dioxide, an aluminum oxide, and alkaline-earth-metal oxide in using for the catalyst for exhaust gas clarification, or using for a silicone rubber filler, it mixes with a titanium dioxide, an aluminum oxide, etc., and it can mix with the usual abrasives, such as rare earth metal oxide and a fluoride, an aluminum oxide, and a zirconium dioxide, and the second cerium of oxidation obtained according to the manufacturing method of this invention can also be used, when using for abrasives.

[0010]

[Example] It explains in full detail in an example and the example of a comparison below. An example 1 high-grade cerium-nitrate solution (northeast metalization study incorporated company make, 99.95% of purity) is dissolved in water, and it is the second cerium  $CeO_2$  of oxidation at 35 degrees C. By conversion, in 1l. of 50g [1. ] cerium-nitrate water solutions, addition mixing of the 1l. of the ammonium bicarbonate water solutions with a concentration of 150g [1. ] was carried out, and 2300g was obtained as precipitate of a 6 corner-guard-like carbonic acid cerium. The obtained precipitate was put into the thermo hygrometer, at 85 degrees C, humidification desiccation processing

was carried out under 95% of relative humidity for 8 hours, and needlelike monochrome oxy-carbonic acid cerium  $\text{Ce}_2\text{O}(\text{CO}_3)_2$  and  $\text{H}_2\text{O}_1$  700g were obtained. This was calcinated at 400 degrees C for 2 hours, and the second cerium of oxidation was obtained. The value from which the property of the second cerium of oxidation and this second cerium of oxidation which were obtained were re-calcinated at 800 degrees C for 5 hours, and specific surface area changed is shown in Table 1.

[0011] In addition, whenever [ yellow / which was shown all over Table 1 ] (YI value) is the value which is the following, and was made and measured. Whenever [ yellow ] shows the degree separated from white in the direction of yellow, and, as for ideal white, whenever [ yellow ] is set to about 0. The numeric value of whenever [ yellow ] becomes large as yellow increases and it keeps away from ideal white. On the occasion of measurement of whenever [ yellow ], the obtained baking object is cracked by the nylon pot (nylon ball) for about 2 hours, and it is made powder 22 micrometers or less by mean-particle-diameter  $d_{50}=2.0^{***}0.2$  micrometer. 5g of this crack \*\*\*\* is packed and measured by no pressurizing in a round-head cel (30mm phix15t) with the Tokyo Denshoku Co., Ltd. make and a color difference meter, each value of XYZ is measured, and it is ASTM. E YI value (whenever [ yellow ]) was calculated according to 313. 3 times per one sample, YI value shown in Table 1 repeated the above-mentioned actuation, measured it 3 times each, and was expressed as a total of 9 times of the averages.

[0012] In example of comparison 1 example 1, humidification desiccation processing of the precipitate of a carbonic acid cerium was not carried out, but it calcinated at 400 degrees C directly for 2 hours, and the second cerium of oxidation was obtained. The other conditions are the same as an example 1. The specific-surface-area value in re-baking is shown in Table 1 for the property of the second obtained cerium of oxidation and 800 degrees C, and 5 hours.

[0013] Sediment of the hexagon-head tabular carbonic acid cerium obtained in the example of comparison 2 example 1 was put into the autoclave, and hydrothermal processing was performed at 120 degrees C for 8 hours. The main things of the obtained product were the shape of 6 corner guards, and a spherical basic carbonic acid cerium ( $\text{Ce}(\text{OH})(\text{CO}_3)$  and  $2\text{H}_2\text{O}$ ), and the amount of generation of a mono-oxy-carbonic acid cerium was about 5% of the whole. This mixture was calcinated at 400 degrees C for 2 hours, and the second cerium of oxidation shown in Table 1 was obtained. Moreover, the specific-surface-area value after re-calcinating at these 800 degrees C for 5 hours is also shown in Table 1.

[0014] Sediment of the hexagon-head tabular carbonic acid cerium obtained in the example of comparison 3 example 1 was put into the thermo hygrometer of installation of steam, and 95% of relative humidity performed humidification heat-treatment at 50 degrees C for 8 hours. Consequently, the mono-oxy-carbonic acid cerium was not obtained, but was still a 6 corner-guard-like carbonic acid cerium. This was calcinated at 400 degrees C for 2 hours, and the second cerium of oxidation shown in Table 1 was obtained, and it re-calcinated at 800 more degrees C for 5 hours, and asked for change of specific surface area.

[0015]

[Table 1]

	400°C × 2時間焼成後		800°C × 5時間再焼成後	
	比表面積( $\text{m}^2/\text{g}$ )	YI値	比表面積( $\text{m}^2/\text{g}$ )	
実施例 1	153	21	15.2	
比較例 1	112	32	2.7	
比較例 2	112	31	2.8	
比較例 3	121	28	5.7	

[0016] In the example duplex ammonium-carbonate water solution, the hexagon-head tabular carbonic acid cerium was obtained on the same conditions as an example 1 except having carried out addition

mixing of the cerium-nitrate water solution. The steam installation oven performed 2300g of this sediment at 95 degrees C, humidification heat-treatment was performed at 95% of relative humidity for 8 hours, and needlelike monochrome oxy-carbonic acid cerium  $\text{Ce}_2\text{O}(\text{CO}_3)_2$  and  $\text{H}_2\text{O}1700\text{g}$  were obtained. This was calcinated at 300 degrees C for 4 hours, and the second cerium of oxidation of the property shown in Table 2 was obtained. Furthermore, this is re-calcinated at 800 degrees C for 5 hours, it asks for change of specific surface area, and the value is shown in Table 2.

[0017] Humidification heat-treatment was not carried out, but the precipitate of the hexagon-head tabular carbonic acid cerium obtained in the example of comparison 4 example 2 was directly calcinated at 300 degrees C for 4 hours, the second cerium of oxidation of the property shown in Table 2 was obtained, the same re-baking processing as an example 2 was performed, and it turned out that it changes to the value of Table 2.

[0018]

[Table 2]

	300°C × 4 時間焼成後		800°C × 5 時間再焼成後	
	比表面積(m <sup>2</sup> /g)	Y I 値	比表面積(m <sup>2</sup> /g)	Y I 値
実施例 2	161	24	13.6	
比較例 4	121	34	2.8	

[0019] The precipitate of the hexagon-head tabular carbonic acid cerium prepared like example 3 example 1 was put into the thermo hygrometer, humidification desiccation processing was performed in 60 degrees C and 90% of relative humidity for 12 hours, and needlelike monochrome oxy-carbonic acid cerium  $\text{Ce}_2\text{O}(\text{CO}_3)_2$  and  $3\text{H}_2\text{O}1800\text{g}$  were obtained. The specific surface area at the time of re-calcinating the property of the second cerium of oxidation and this second cerium of oxidation which calcinated the obtained mono-oxy-carbonic acid cerium at 500 degrees C for 2 hours, and were obtained at 800 degrees C for 5 hours is shown in Table 3.

[0020] Although the precipitate of the hexagon-head tabular carbonic acid cerium prepared like example of comparison 5 example 1 was put into the thermo hygrometer and humidification desiccation processing was performed in 60 degrees C and 70% of relative humidity for 12 hours, the mono-oxy-carbonic acid cerium was not obtained, but was still a 6 corner-guard-like carbonic acid cerium. The specific surface area at the time of re-calcinating the property of the second cerium of oxidation and this second cerium of oxidation which calcinated this carbonic acid cerium at 500 degrees C for 2 hours, and were obtained at 800 degrees C for 5 hours is shown in Table 3.

[0021]

[Table 3]

	500°C × 2 時間焼成後		800°C × 5 時間再焼成後	
	比表面積(m <sup>2</sup> /g)	Y I 値	比表面積(m <sup>2</sup> /g)	Y I 値
実施例 3	142	19	14.7	
比較例 5	103	28	3.1	

[0022] Sediment of the hexagon-head tabular carbonic acid cerium prepared like example 4 example 2 was put into the oven which introduced steam, humidification desiccation processing was performed in 85 degrees C and 80% of relative humidity for 8 hours, and needlelike mono-oxy-carbonic acid cerium 1700g was obtained. The specific surface area at the time of re-calcinating the property of the second cerium of oxidation and the second cerium of oxidation which calcinated obtained mono-oxy-carbonic acid cerium  $\text{Ce}_2\text{O}(\text{CO}_3)_2$  and  $\text{H}_2\text{O}$  at 500 degrees C for 2 hours, and were obtained at 800 degrees C for 5 hours is shown in Table 4.

[0023] Although sediment of the hexagon-head tabular carbonic acid cerium prepared like example of comparison 6 example 2 was put into the oven which introduced steam and humidification desiccation processing was performed in 85 degrees C and 70% of relative humidity for 8 hours, the mono-oxy-carbonic acid cerium was not obtained, but was still a 6 corner-guard-like carbonic acid cerium. The specific surface area at the time of re-calcinating the property of the second cerium of oxidation and this second cerium of oxidation which calcinated this carbonic acid cerium at 500 degrees C for 2 hours, and were obtained at 800 degrees C for 5 hours is shown in Table 4.

[0024] It put into the oven which placed the bat which filled water in the pars basilaris ossis occipitalis for sediment of the hexagon-head tabular carbonic acid cerium prepared like example of comparison 7 example 2, and humidification desiccation processing was performed for 8 hours in the water vapor pressure equivalent to 110 degrees C and 85% of relative humidity. The amount of generation of the mono-oxy-carbonic acid cerium which the carbonic acid cerium which the main products in this case are hexagon-head tabular and a spherical basic carbonic acid cerium salt, in addition maintained about 20% of unreacted hexagon-head tabular is accepted, and is made into the purpose was about 5% of the whole. The specific surface area at the time of re-calcinating the property of the second cerium of oxidation and this second cerium of oxidation which calcinated the obtained mixture at 500 degrees C for 2 hours, and were obtained at 800 degrees C for 5 hours is shown in Table 4.

[0025]

[Table 4]

	500°C × 2時間焼成後		800°C × 5時間再焼成後	
	比表面積(m <sup>2</sup> /g)	Y I 値	比表面積(m <sup>2</sup> /g)	Y I 値
実施例4	147	18	14.8	
比較例6	96	27	2.7	
比較例7	105	26	4.9	

[0026]

[Effect of the Invention] the second cerium of oxidation obtained in this invention -- the second conventional cerium of oxidation -- comparing -- I -- there are few falls of the specific surface area in the RO high temperature which has a big specific surface area.

c) Present the color tone near white.

There is effectiveness of \*\*\*\*\*. Moreover, by the manufacture approach of this invention, the second cerium of oxidation of this invention which has the aforementioned property can be manufactured often [ repeatability ] and easily. Therefore, the second cerium of oxidation obtained by this invention fits especially the second cerium of oxidation with which heat-resistant stability is demanded like the catalyst for exhaust gas clarification, and a silicone rubber filler.

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**TECHNICAL FIELD**

---

**[Industrial Application]** This invention relates to offering in detail the second cerium of oxidation by which the fall of specific surface area was stabilized few also in the high temperature field, and the second cerium of oxidation near white as a color tone about the manufacture approach of the second cerium of oxidation.

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**PRIOR ART**

[Description of the Prior Art] Conventionally, the second cerium of oxidation is used in large quantities as the catalyst for exhaust gas clarification, a silicone rubber filler, abrasives, etc., for example, is set in the catalyst field. Absorb oxygen by the oxidizing atmosphere and the property of the second cerium of oxidation of emitting oxygen by reducing atmosphere is used. HC, CO, and NOx It is used as an additive which raises thermal resistance, without performing receiving improvement in the rate of purification, and reducing rubber reinforcement in a silicone rubber filler. Such second conventional cerium of oxidation is manufactured by the approach of adding oxalic acid or ammonium bicarbonate in the nitrate solution or hydrochloride solution of a cerium, and usually washing, drying and calcinating the precipitate obtained a RO exception etc. However, although the second conventional cerium of oxidation manufactured by said approach etc. had the specific surface area about 100m<sup>2</sup> / g, when [ in which specific surface area falls to below 10m<sup>2</sup> / g by 800 degree-C baking ] adding and using it for silicone rubber further, since whenever [ yellow / of the second cerium of oxidation ] was high, it had the fault that the color of rubber came seemingly to be yellow. Moreover, since the polish capacity of the second cerium of oxidation used for abrasives is greatly influenced by the mechanochemical part (surface activity), high specific-surface-area-ization in the about 800-1000-degree C usual burning-temperature region is desired.

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**EFFECT OF THE INVENTION**

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[Effect of the Invention] the second cerium of oxidation obtained in this invention -- the second conventional cerium of oxidation -- comparing -- I -- there are few falls of the specific surface area in the RO high temperature which has a big specific surface area.

c) Present the color tone near white.

There is effectiveness of \*\*\*\*\*. Moreover, by the manufacture approach of this invention, the second cerium of oxidation of this invention which has the aforementioned property can be manufactured often [ repeatability ] and easily. Therefore, the second cerium of oxidation obtained by this invention fits especially the second cerium of oxidation with which heat-resistant stability is demanded like the catalyst for exhaust gas clarification, and a silicone rubber filler.

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**TECHNICAL PROBLEM**

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**[Problem(s) to be Solved by the Invention]** In order to use for the above applications and to raise the engine performance etc. further, it is required that a color tone should be brought close to white at the thing list whose fall of a still higher specific surface area and the specific surface area in an elevated temperature is stable few as a property of the second cerium of oxidation.

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MEANS

[Means for Solving the Problem] As a result of examining many things that the above-mentioned technical problem should be solved, after this invention person performed humidification heat-treatment in the 60-100-degree C temperature requirement and used the carbonic acid cerium as the mono-oxy-carbonic acid cerium under high humidity of 80% or more of relative humidity, he found out the manufacture approach of the second cerium of oxidation characterized by calcinating.

[0005] First, it describes about the carbonic acid cerium which is a raw material. The carbonic acid cerium is marketed and it can also perform using it in this invention. It is as follows supposing an example which manufactures a carbonic acid cerium is shown. That is, a cerium-nitrate water solution and an ammonium bicarbonate water solution are mixed first, and carbonic acid cerium precipitate is obtained. Under the present circumstances, a mixed sequence foreword may add an ammonium bicarbonate water solution in a cerium-nitrate water solution, or may carry out addition mixing of the cerium-nitrate water solution at an ammonium bicarbonate water solution. 30-200g /of concentration of this cerium-nitrate water solution is [ 1. ] the range of 100-150g/l. especially preferably preferably.

Moreover, as for the mixed rate of a cerium-nitrate water solution and an ammonium bicarbonate water solution, it is desirable that it is the range of 1:1.4-3 in the weight ratio of the cerium nitrate contained in each water solution and ammonium bicarbonate. Under the present circumstances, the carbonic acid ceriums obtained are  $Ce_2 3 (CO_3)$  and  $xH_2 O$  ( $x=1-8$ ) in a trivalent cerium.

[0006] This invention next performs humidification heat-treatment for the carbonic acid cerium obtained as mentioned above or a commercial thing under high humidity of 80% or more of relative humidity in a 60-100-degree C temperature requirement. By this processing, a needlelike or spherical mono-oxy-carbonic acid cerium [ $Ce_2 O(CO_3)_2$  and  $xH_2 O$  ( $x=1-6$ )] generates from a 6 corner-guard-like carbonic acid cerium.

[0007] The oven which introduced a thermo hygrometer and steam can perform the above-mentioned humidification heat-treatment, and the processing time has 1 desirable hours or more. Since the generation rate of a mono-oxy-carbonic acid cerium will fall probably because the desorption for surface water arises and most will serve as basic carbonates, such as  $Ce(OH)_2 (CO_3)$  and  $xH_2 O$ , before desorption of water of crystallization if a mono-oxy-carbonic acid cerium does not generate but 100 degrees C is exceeded probably because water of crystallization cannot \*\*\*\* easily when the temperature of humidification desiccation processing is less than 60 degrees C, it is necessary to consider as the above-mentioned temperature requirement. Moreover, since an amorphous part appears from a carbonic acid cerium like [ if relative humidity is less than 80%, probably because the amount of surface water will \*\*\*\* before desorption of water of crystallization ] the usual desiccation processing, it is not desirable.

[0008] Next, although the second cerium of oxidation is obtained by calcinating the mono-oxy-carbonic acid cerium made to generate, it is 300-550 degrees C more preferably, and 1 - 4 hours of firing time are desirable [ this burning temperature has desirable 300-650 degrees C, and ]. It is completely  $CeO_2$  even if it lengthens firing time, when burning temperature is less than 300 degrees C.  $CeO_2$  obtained when it was hard to change and 550 degrees C was exceeded Since specific surface area is small in comparison,

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[0009] The second cerium of oxidation obtained in this invention has more than 140m<sup>2</sup> / g, and a large specific surface area, and it has an elevated temperature and at least 700 degrees C or more of properties with especially few falls of specific surface area, and is the thing of the high color tone of a whiteness degree. Moreover, that configuration is also a needle, a globular shape, a cube, etc., in the case of a globular shape and a cube, a path and one side are 20 micrometers or less, respectively, and when needlelike, a size is not limited for them to this value, although 10 micrometers or less and die length have [ three or more ] 60 micrometers and a common aspect ratio. Even if it remains as it is, it can also be used, but in mixing with a zirconium dioxide, an aluminum oxide, and alkaline-earth-metal oxide in using for the catalyst for exhaust gas clarification, or using for a silicone rubber filler, it mixes with a titanium dioxide, an aluminum oxide, etc., and it can mix with the usual abrasives, such as rare earth metal oxide and a fluoride, an aluminum oxide, and a zirconium dioxide, and the second cerium of oxidation obtained according to the manufacturing method of this invention can also be used, when using for abrasives.

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EXAMPLE

[Example] It explains in full detail in an example and the example of a comparison below. An example 1 high-grade cerium-nitrate solution (northeast metalization study incorporated company make, 99.95% of purity) is dissolved in water, and it is the second cerium CeO<sub>2</sub> of oxidation at 35 degrees C. By conversion, in 1l. of 50g [1. ] cerium-nitrate water solutions, addition mixing of the 1l. of the ammonium bicarbonate water solutions with a concentration of 150g [1. ] was carried out, and 2300g was obtained as precipitate of a 6 corner-guard-like carbonic acid cerium. The obtained precipitate was put into the thermo hygrostat, at 85 degrees C, humidification desiccation processing was carried out under 95% of relative humidity for 8 hours, and needlelike monochrome oxy-carbonic acid cerium Ce<sub>2</sub>O(CO<sub>3</sub>)<sub>2</sub> and H<sub>2</sub>O<sub>1700</sub>g were obtained. This was calcinated at 400 degrees C for 2 hours, and the second cerium of oxidation was obtained. The value from which the property of the second cerium of oxidation and this second cerium of oxidation which were obtained were re-calcinated at 800 degrees C for 5 hours, and specific surface area changed is shown in Table 1.

[0011] In addition, whenever [ yellow / which was shown all over Table 1 ] (YI value) is the value which is the following, and was made and measured. Whenever [ yellow ] shows the degree separated from white in the direction of yellow, and, as for ideal white, whenever [ yellow ] is set to about 0. The numeric value of whenever [ yellow ] becomes large as yellow increases and it keeps away from ideal white. On the occasion of measurement of whenever [ yellow ], the obtained baking object is cracked by the nylon pot (nylon ball) for about 2 hours, and it is made powder 22 micrometers or less by mean-particle-diameter d<sub>50</sub>=2.0\*\*0.2micrometer. 5g of this crack \*\*\*\* is packed and measured by no pressurizing in a round-head cel (30mm phix15t) with the Tokyo Denshoku Co., Ltd. make and a color difference meter, each value of XYZ is measured, and it is ASTM. E YI value (whenever [ yellow ]) was calculated according to 313. 3 times per one sample, YI value shown in Table 1.repeated the above-mentioned actuation, measured it 3 times each, and was expressed as a total of 9 times of the averages.

[0012] In example of comparison 1 example 1, humidification desiccation processing of the precipitate of a carbonic acid cerium was not carried out, but it calcinated at 400 degrees C directly for 2 hours, and the second cerium of oxidation was obtained. The other conditions are the same as an example 1. The specific-surface-area value in re-baking is shown in Table 1 for the property of the second obtained cerium of oxidation and 800 degrees C, and 5 hours.

[0013] Sediment of the hexagon-head tabular carbonic acid cerium obtained in the example of comparison 2 example 1 was put into the autoclave, and hydrothermal processing was performed at 120 degrees C for 8 hours. The main things of the obtained product were the shape of 6 corner guards, and a spherical basic carbonic acid cerium (Ce(OH)<sub>2</sub>CO<sub>3</sub> and 2H<sub>2</sub>O), and the amount of generation of a mono-oxy-carbonic acid cerium was about 5% of the whole. This mixture was calcinated at 400 degrees C for 2 hours, and the second cerium of oxidation shown in Table 1 was obtained. Moreover, the specific-surface-area value after re-calcinating at these 800 degrees C for 5 hours is also shown in Table 1.

[0014] Sediment of the hexagon-head tabular carbonic acid cerium obtained in the example of comparison 3 example 1 was put into the thermo hygrostat of installation of steam, and 95% of relative

humidity performed humidification heat-treatment at 50 degrees C for 8 hours. Consequently, the mono-oxy-carbonic acid cerium was not obtained, but was still a 6 corner-guard-like carbonic acid cerium. This was calcinated at 400 degrees C for 2 hours, and the second cerium of oxidation shown in Table 1 was obtained, and it re-calcinated at 800 more degrees C for 5 hours, and asked for change of specific surface area.

[0015]

[Table 1]

	400°C × 2時間焼成後	800°C × 5時間再焼成後	
	比表面積(m <sup>2</sup> /g)	Y I 値	比表面積(m <sup>2</sup> /g)
実施例 1	153	21	15.2
比較例 1	112	32	2.7
比較例 2	112	31	2.8
比較例 3	121	28	5.7

[0016] In the example duplex ammonium-carbonate water solution, the hexagon-head tabular carbonic acid cerium was obtained on the same conditions as an example 1 except having carried out addition mixing of the cerium-nitrate water solution. The steam installation oven performed 2300g of this sediment at 95 degrees C, humidification heat-treatment was performed at 95% of relative humidity for 8 hours, and needlelike monochrome oxy-carbonic acid cerium Ce<sub>2</sub>O(CO<sub>3</sub>)<sub>2</sub> and H<sub>2</sub>O<sub>1700</sub>g were obtained. This was calcinated at 300 degrees C for 4 hours, and the second cerium of oxidation of the property shown in Table 2 was obtained. Furthermore, this is re-calcinated at 800 degrees C for 5 hours, it asks for change of specific surface area, and the value is shown in Table 2.

[0017] Humidification heat-treatment was not carried out, but the precipitate of the hexagon-head tabular carbonic acid cerium obtained in the example of comparison 4 example 2 was directly calcinated at 300 degrees C for 4 hours, the second cerium of oxidation of the property shown in Table 2 was obtained, the same re-baking processing as an example 2 was performed, and it turned out that it changes to the value of Table 2.

[0018]

[Table 2]

	300°C × 4時間焼成後	800°C × 5時間再焼成後	
	比表面積(m <sup>2</sup> /g)	Y I 値	比表面積(m <sup>2</sup> /g)
実施例 2	161	24	13.6
比較例 4	121	34	2.8

[0019] The precipitate of the hexagon-head tabular carbonic acid cerium prepared like example 3 example 1 was put into the thermo hygrostat, humidification desiccation processing was performed in 60 degrees C and 90% of relative humidity for 12 hours, and needlelike monochrome oxy-carbonic acid cerium Ce<sub>2</sub>O(CO<sub>3</sub>)<sub>2</sub> and 3H<sub>2</sub>O<sub>1800</sub>g were obtained. The specific surface area at the time of re-calcinating the property of the second cerium of oxidation and this second cerium of oxidation which calcinated the obtained mono-oxy-carbonic acid cerium at 500 degrees C for 2 hours, and were obtained at 800 degrees C for 5 hours is shown in Table 3.

[0020] Although the precipitate of the hexagon-head tabular carbonic acid cerium prepared like example of comparison 5 example 1 was put into the thermo hygrostat and humidification desiccation processing was performed in 60 degrees C and 70% of relative humidity for 12 hours, the mono-oxy-carbonic acid cerium was not obtained, but was still a 6 corner-guard-like carbonic acid cerium. The specific surface

area at the time of re-calcinating the property of the second cerium of oxidation and this second cerium of oxidation which calcinated this carbonic acid cerium at 500 degrees C for 2 hours, and were obtained at 800 degrees C for 5 hours is shown in Table 3.

[0021]

[Table 3]

	500°C × 2時間焼成後		800°C × 5時間再焼成後	
	比表面積(m <sup>2</sup> /g)	Y I 値	比表面積(m <sup>2</sup> /g)	
実施例3	142	19	14.7	
比較例5	103	28	3.1	

[0022] Sediment of the hexagon-head tabular carbonic acid cerium prepared like example 4 example 2 was put into the oven which introduced steam, humidification desiccation processing was performed in 85 degrees C and 80% of relative humidity for 8 hours, and needlelike mono-oxy-carbonic acid cerium 1700g was obtained. The specific surface area at the time of re-calcinating the property of the second cerium of oxidation and the second cerium of oxidation which calcinated obtained mono-oxy-carbonic acid cerium Ce<sub>2</sub>O(CO<sub>3</sub>)<sub>2</sub> and H<sub>2</sub>O at 500 degrees C for 2 hours, and were obtained at 800 degrees C for 5 hours is shown in Table 4.

[0023] Although sediment of the hexagon-head tabular carbonic acid cerium prepared like example of comparison 6 example 2 was put into the oven which introduced steam and humidification desiccation processing was performed in 85 degrees C and 70% of relative humidity for 8 hours, the mono-oxy-carbonic acid cerium was not obtained, but was still a 6 corner-guard-like carbonic acid cerium. The specific surface area at the time of re-calcinating the property of the second cerium of oxidation and this second cerium of oxidation which calcinated this carbonic acid cerium at 500 degrees C for 2 hours, and were obtained at 800 degrees C for 5 hours is shown in Table 4.

[0024] It put into the oven which placed the bat which filled water in the pars basilaris ossis occipitalis for sediment of the hexagon-head tabular carbonic acid cerium prepared like example of comparison 7 example 2, and humidification desiccation processing was performed for 8 hours in the water vapor pressure equivalent to 110 degrees C and 85% of relative humidity. The amount of generation of the mono-oxy-carbonic acid cerium which the carbonic acid cerium which the main products in this case are hexagon-head tabular and a spherical basic carbonic acid cerium salt, in addition maintained about 20% of unreacted hexagon-head tabular is accepted, and is made into the purpose was about 5% of the whole. The specific surface area at the time of re-calcinating the property of the second cerium of oxidation and this second cerium of oxidation which calcinated the obtained mixture at 500 degrees C for 2 hours, and were obtained at 800 degrees C for 5 hours is shown in Table 4.

[0025]

[Table 4]

	500°C × 2時間焼成後		800°C × 5時間再焼成後	
	比表面積(m <sup>2</sup> /g)	Y I 値	比表面積(m <sup>2</sup> /g)	
実施例4	147	18	14.8	
比較例6	96	27	2.7	
比較例7	105	26	4.9	

[Translation done.]